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13. ABSTRACT (Maximum 200 Words) A variety of approaches have been taken to enhance GaN quality during epitaxy and lead zirconate titanate (PZT) structures for sensors and data storage. GaN regrown on KOH etched templates with defective material removed has shown improved optical quality and demonstrated lateral growth by MBE. The same also carried out using MOCVD. GaN layers were also grown on closely lattice and stacking matched ZnO substrates. In this vein, we developed a high temperature thermal treatment for ZnO substrate. After 3 hours annealing in the air at 1050°C, all the surface damages were removed and straight, parallel terrace features were formed on the surface as judged by AFM images, which can facilitate smooth 2D growth and reduce column formation during the growth of GaN epilayers without the deleterious effects of a damaged substrate surface. Thin films of PZT were grown by sol-gel techniques on sapphire, Pt/Ti/SiO <sub>2</sub> /Si and Ir/Ti/SiO <sub>2</sub> /Si. For electrical characterization, the top electrodes for Au/PZT/Pt and Au/PZT/Ir capacitors were fabricated by photolithography and liftoff process. The polarization hysteresis and fatigue characteristics were measured by using a ferroelectric tester.				
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## Contract Information

Contract Number	N00014-01-1-0038
Title of Research	Growth and investigation of a class of ferroelectric oxides for multifunctional devices
Principal Investigator	Hadis Morkoc
Organization	Virginia Commonwealth University

## Technical Section

### *Technical Objectives*

Growth and characterization of a class of ferroelectric oxides for multifunctional device applications.

### *Technical Approach*

In order to apply lead zirconate titanate (PZT) to functional devices such as sensors, surface acoustic wave (SAW) devices, and metal ferroelectric semiconductor field effect transistors (MFSFETs) by utilizing wide band gap semiconductors such as GaN, ZnO. As essential steps, PZT thin films with various compositions (Pb:Zr:Ti ratio) were grown by sol-gel techniques on various substrates, including sapphire, Pt/Ti/SiO<sub>2</sub>/Si and Ir/Ti/SiO<sub>2</sub>/Si substrates. For electrical characterization, the top electrodes for Au/PZT/Pt and Au/PZT/Ir capacitors were fabricated by photolithography and liftoff process, The Ir bottom electrodes were obtained through a collaboration with Samsung Advanced Institute of Technology. The photolithography and wet etching conditions (HF, HF:H<sub>2</sub>O<sub>2</sub>:HNO<sub>3</sub>) were optimized to explore multifunctional device applications. The polarization hysteresis and fatigue characteristics were measured by using a ferroelectric tester.

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## Progress

### 1. Electrical characterization of sol-gel PZT

The Sol-gel method is cost effective and allows the compositions of PZT thin films to be changed with ease. We investigated sol-gel method and optimized the associated process parameters such as spin-coating, dry, hydrolysis, and annealing. PZT films were prepared using sol-gel method on Pt(111)/TiO<sub>2</sub>/SiO<sub>2</sub>/Si substrates or Ir(111)/Ti/SiO<sub>2</sub>/Si substrates. The film deposition was performed by spin-coating of PZT precursor at 4000 rpm for 40 s and then dried at 200°C on a hot plate for 5 min. These steps were repeated until the desired film thickness (180 nm) was obtained. The films were then pyrolyzed at various temperatures ranging from 300°C to 400°C in order to remove the residual organic species, and then finally they were crystallized at higher temperatures in a preheated furnace in O<sub>2</sub> ambient.

To fabricate capacitor structures (Au/PZT/Pt and Au/PZT/Ir), 1000Å thick Au top electrode was deposited by thermal evaporation. For wet etching of PZT, 48% HF was normally used. For future multifunctional device applications such as sensors and metal ferroelectric semiconductor field effect transistor (MFSFET) fabrication processes need to be developed. In this vein HF: H<sub>2</sub>O<sub>2</sub>:HNO<sub>3</sub> = 1:30:1 etchant was found to exhibit the required selectivity. It was also found that a Au/Cr bilayer could be used to improve the adhesion of top electrode to PZT. Electrical measurements in terms of polarization hysteresis, and fatigue were conducted by using a ferroelectric tester (Radiant tech. Precision LC).

Figure 1 (a) and (b) show the polarization hysteresis of Au/PZT/Pt capacitor (denoted as SGPZT\_I) with varying sweep voltage. The PZT film was annealed at 700°C for 10 min in air before Au evaporation. In Figure 1(a), the sweep voltage varies from ±1 to ±7 V, and one can see the polarization saturation at around ±5V. The maximum polarization ( $P_{\max}$ ) was 30.6  $\mu\text{C}/\text{cm}^2$ , the remnant polarization ( $P_r$ ) was 20  $\mu\text{C}/\text{cm}^2$ , and coercive voltage ( $E_c$ ) was 1.5 V (equivalently, 100 kV/cm). In Figure 1(b) represents a wider range of sweep voltages between ±20 V. It turned out that the capacitor functions up to ±18 V. It, however, failed at ±20V (see leakage current at -20V).

Figure 2 shows the  $P_{\max}$ ,  $P_r$  and  $E_c$  at various sweep voltages. Throughout the range of 5 - 15V, a saturated  $P_r \approx 26 \mu\text{C}/\text{cm}^2$  and an  $E_c \approx 1.5\text{V}$  were obtained. Figure 3 shows the polarization hysteresis of Au/PZT/Pt capacitor RTA annealed at 750°C for 10s (denoted as SGPZT\_II) (the anneal temperature is 50°C higher and anneal time was much shorter than that used for SGPZT\_I). It can be seen that the polarization does not saturate even up to ±11 V, and leaky capacitor features appear at -11 V. Figure 4 shows the polarization hysteresis of Au/PZT/Ir (denoted as SGPZT\_III) which was RTA annealed at 550°C for 30 min, (150°C lower temperature and 20 min longer anneal time than SGPZT\_I). One can see that the polarization does not saturate and the coercive voltage is larger than that for SGPZT\_I, indicating that the anneal time of 10s was relatively short and the anneal temperature of 550°C was relatively low for ferroelectric capacitor fabrication.

Figure 5 shows the polarization change ( $dP/dV$ ) of sample SGPZT\_I, II, and III as a function of sweep voltage. It can be seen that the  $dP/dV$  of SGPZT\_III shows a sharp/narrow peak at a certain voltage (coercive voltage) while the coercive voltage of SGPZT\_III is larger than those for SGPZT\_I and II. This may imply that statistically most ferroelectric domains in SGPZT\_III are more readily switched at the coercive voltage compared to SGPZT\_I and II.

Since we used Ir substrate only for SGPZT\_III, it is tempting to suggest that this feature may in some way be related to the substrate, i.e. Pt vs. Ir.

Figure 6 shows the polarization hysteresis curves of Au/PZT/Ir at different furnace anneal temperatures in air for 30min: 550 °C (sample SGPZT\_IV), 600 °C (SGPZT\_V), 650 °C, and 700 °C (SGPZT\_VI). A polarization gap at 0 V especially for the samples annealed at high temperatures (650, 700 °C) was observed. It has been reported that the gap may be related to oxygen vacancies at Au/PZT and/or PZT/Ir interface [Appl. Phys. Lett. 69, 2540 (1996)]. In order to reduce the oxygen vacancies, the three samples under investigation were annealed again in oxygen/Ar mixture at 700 °C for 10 min. Figure 7(a), (b) and (c) compare the normalized polarization hysteresis curves before and after annealing of SGPZT\_IV, V, and VI, respectively. It is seen that after annealing the polarization gap at 0 V was reduced and also the coercive voltage decreased dramatically for all three samples, which might be related to defects (e.g. oxygen vacancies), annihilation at PZT film/Pt bottom electrode, and/or PZT/Au top electrode interface.

The polarization hysteresis curves of PZT on Pt/Ti/SiO<sub>2</sub>/Si and PZT on Ir/Ti/SiO<sub>2</sub>/Si substrates have been compared. Figure 8(a) shows the polarization hysteresis of Au/PZT/Pt annealed at 600 °C for 10 min (denoted SGPZT\_VII). The sweep voltage varied from  $\pm 3$  V to  $\pm 8$  V and beyond  $\pm 5$  V the polarization saturated and at 5 V,  $P_{\max} = 33.3 \mu\text{C}/\text{cm}^2$ ,  $P_r = 17.1 \mu\text{C}/\text{cm}^2$ , and  $E_c = 1.26$  V (84 kV/cm). Figure 8 (b) shows the fatigue (degradation) properties of SGPZT\_VII with the standard positive up negative down (PUND) test. [http://www.ferrodevices.com]. The PUND stress frequency is  $10^6$  Hz. It is seen that after  $10^{10}$  cycles the polarization decreased to about 60% of the initial value, while as shown in Figure 9(a) the Au/PZT/Ir annealed at 600 °C for 10 min (denoted SGPZT\_VIII) has  $P_{\max} = 41.1 \mu\text{C}/\text{cm}^2$ ,  $P_r = 22.7 \mu\text{C}/\text{cm}^2$ , and  $E_c = 1.5$  V (100.7 kV/cm) at 5 V. Figure 9 (b) represents the PUND test result for SGPZT\_VIII. Up to  $10^8$  cycles no noticeable degradation is observed. One of the well-known degradation mechanism of PZT grown on Pt is oxygen vacancy accumulation at the PZT/Pt (top and/or bottom electrode) interface. In this vein, the PZT/Ir interface may offer better resistance to oxygen accumulation and thus better fatigue properties could be obtained. Further understanding about the degradation mechanism and investigations of fatigue free electrode such as RuO<sub>2</sub>, LSCO (La<sub>0.5</sub> Sr<sub>0.5</sub>CoO<sub>3</sub>), SrRuO<sub>3</sub>, hybrid Ir/IrO<sub>2</sub> are needed for near future multifunctional device applications.

## 2. Works in progress:

(1) Using STO buffer layers, the PZT/STO/ Pt/TiO<sub>2</sub>/SiO<sub>x</sub>/Si are being grown. We have grown several samples and are in the process of optimizing the growth conditions in order to get excellent electrical properties such as low coercive voltage, high remnant polarization, fatigue free capacitors, etc. (2) We have started to work on realizing lateral polarization on PZT thin films, which may be highly sensitive to irradiation by light or humidity compared to vertical polarization in PZT thin films. This aspect can be utilized for sensors. We plan to use sol-gel solutions of Pb(Zn<sub>0.2</sub>Ti<sub>0.8</sub>)O<sub>3</sub> and La-doped PbLaZnTiO<sub>3</sub> (PLZT) to optimize horizontal polarization. (3) One of the main tasks now is to grow high quality thin films with enhanced repeatability and uniformity. Next work is to make multi-function devices e.g. multifunctional sensors utilizing surface acoustic wave (SAW) principle or metal ferroelectric semiconductor field effect transistor (MFSFET) using wide bandgap semiconductors such as GaN, ZnO and

SiC. In terms of the deposition, all the components and parts needed for growing PZT films by MBE are in place. As soon as the work being done in the MBE system slated for this work is transferred to a new II-VI MBE, the system will be available and used for PZT investigations. The aim is to ascertain whether films with better polarization features and fatigue characteristics could be obtained.

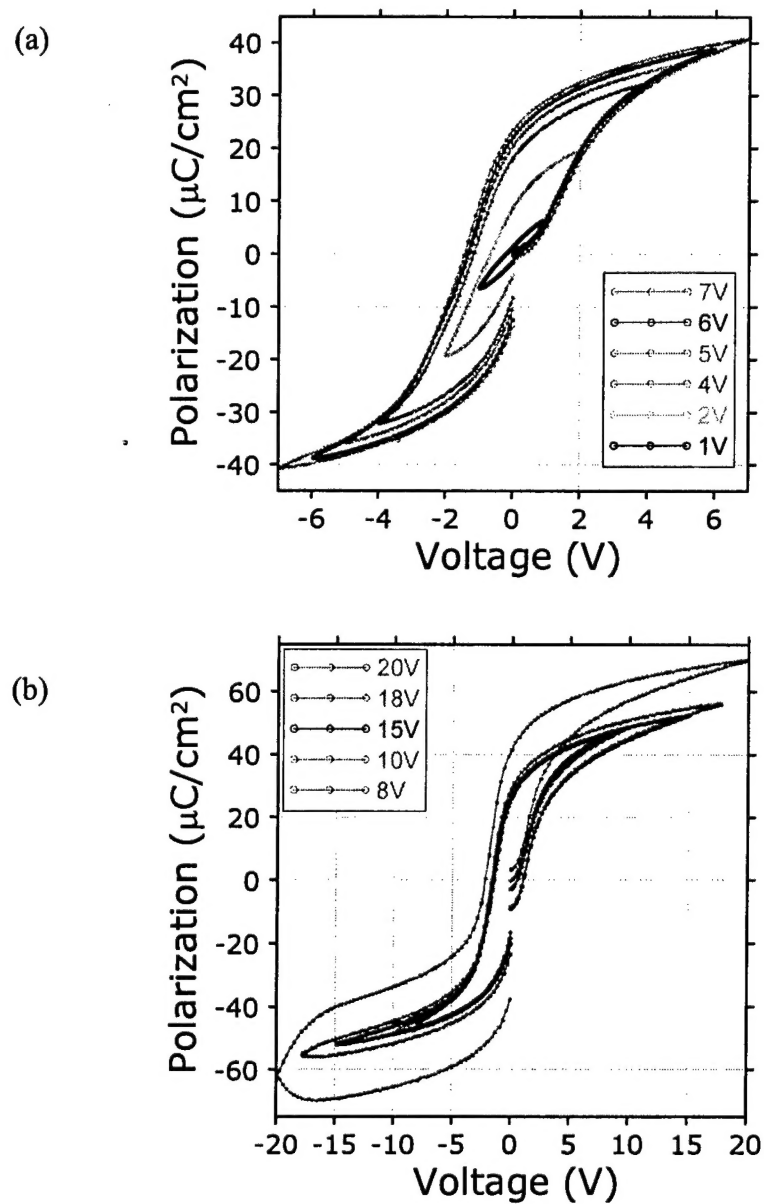


Figure 1(a). Polarization hysteresis loops of Au/PZT/Pt (700°C, 10 min RTA in air) at various sweep voltage  $\pm 1, \pm 2, \pm 4, \pm 5, \pm 6, \pm 7$  V. (b) Sweep voltage  $\pm 8, \pm 10, \pm 15, \pm 18, \pm 20$  V.

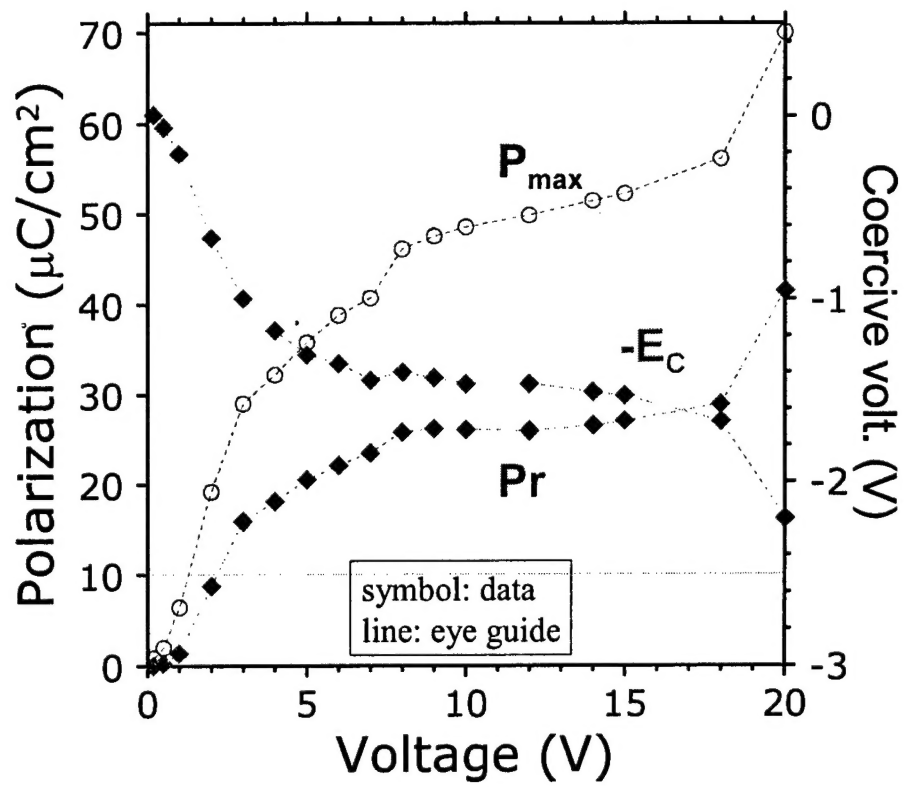


Figure 2. Maximum polarization ( $P_{max}$ ), remnant polarization ( $P_r$ ), and coercive voltage ( $E_c$ ) at various sweep voltage.

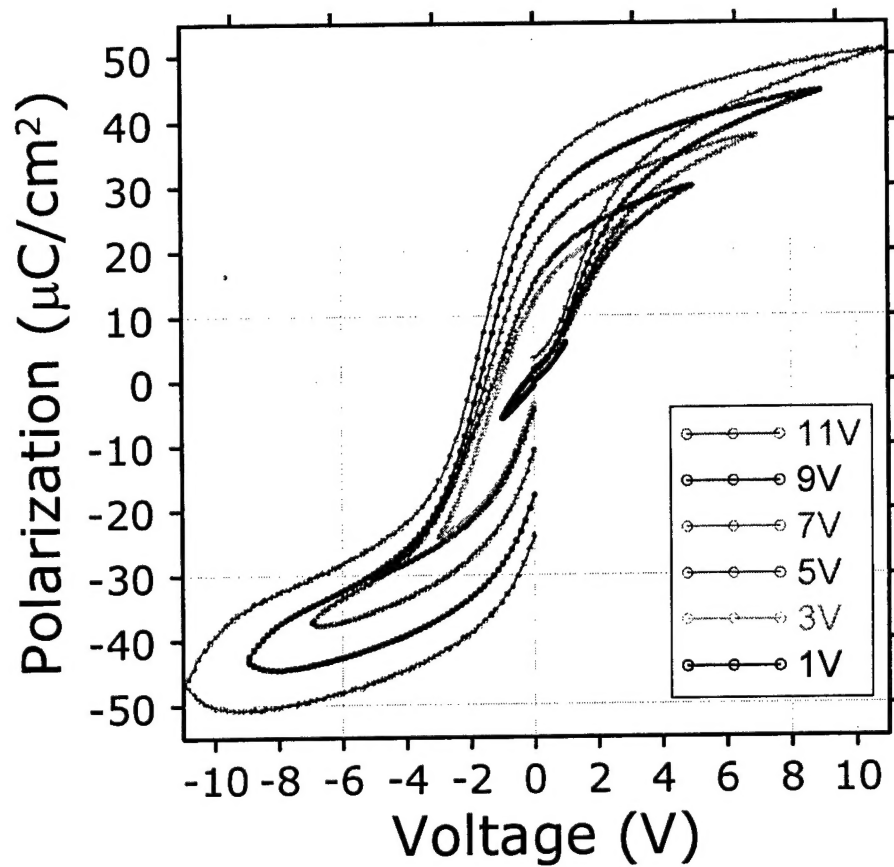


Figure 3. Polarization hysteresis loops of Au/PZT/Pt (750°C, 10 s RTA in air) at various sweep voltage  $\pm 1$ ,  $\pm 3$ ,  $\pm 5$ ,  $\pm 7$ ,  $\pm 9$ ,  $\pm 11$  V.

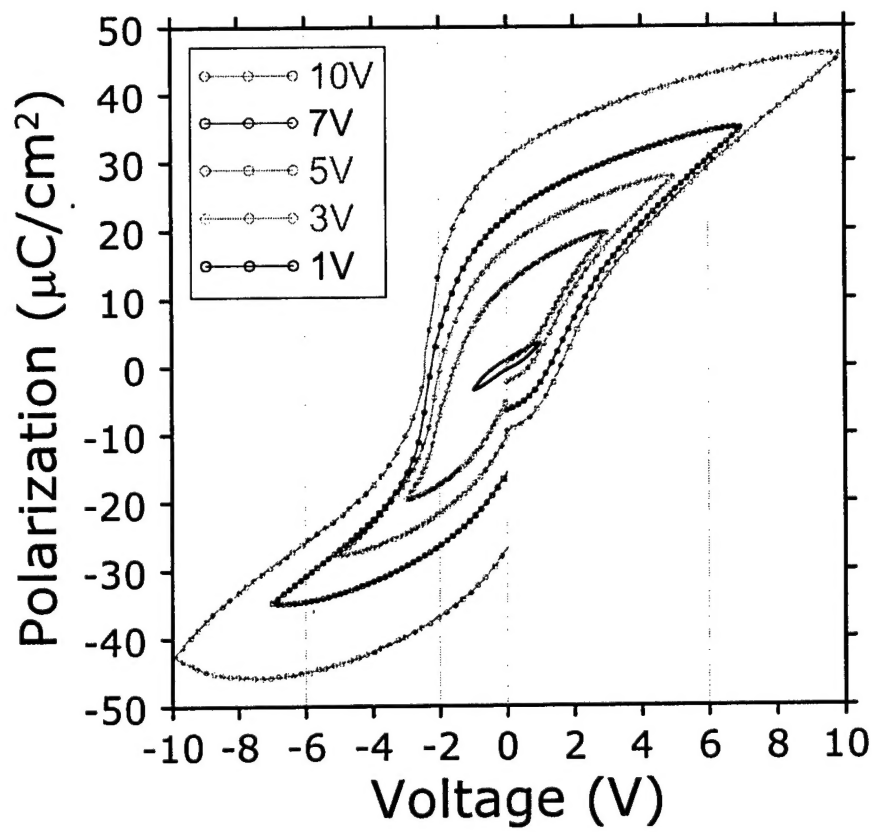


Figure 4. Polarization hysteresis loops of Au/PZT/Ir (550°C, 30 min furnace anneal in air) at various sweep voltage  $\pm 1$ ,  $\pm 3$ ,  $\pm 5$ ,  $\pm 7$ ,  $\pm 10$  V.

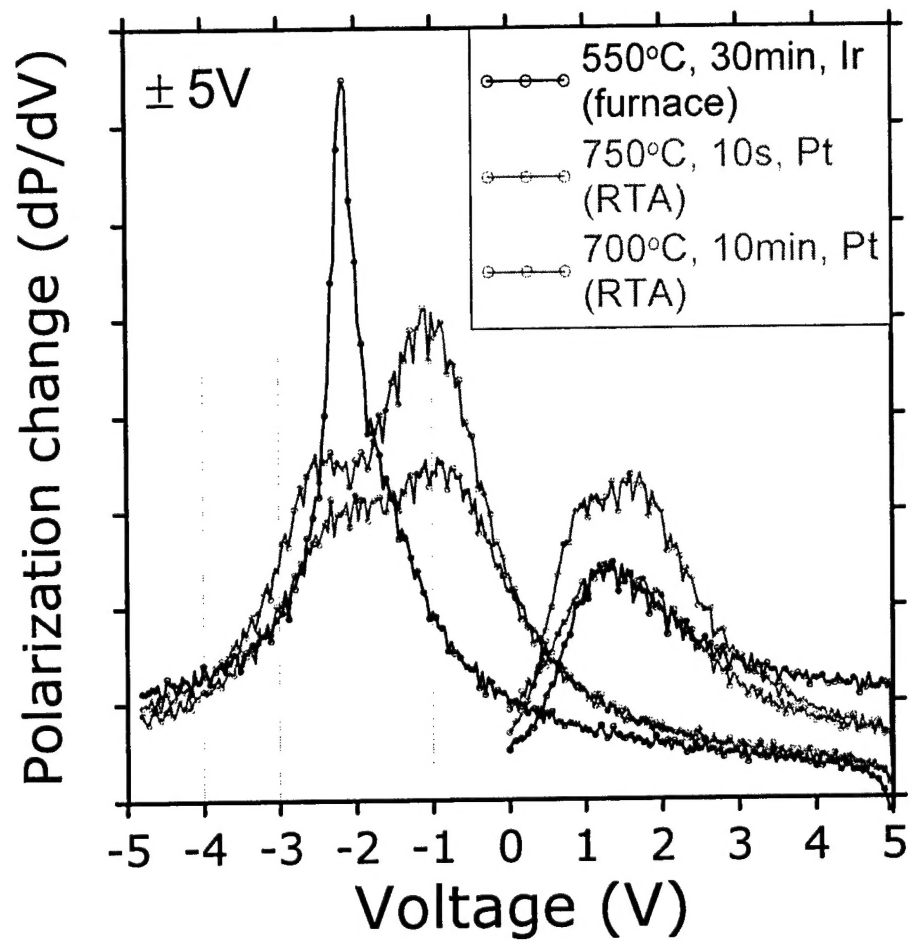


Figure 5. Polarization change ( $dP/dV$ ) vs. voltage of Au/PZT/Ir (550°C, 30 min furnace anneal in air), Au/PZT/Pt (700°C, 10 min RTA in air), and Au/PZT/Pt (750°C, 10 s RTA in air).

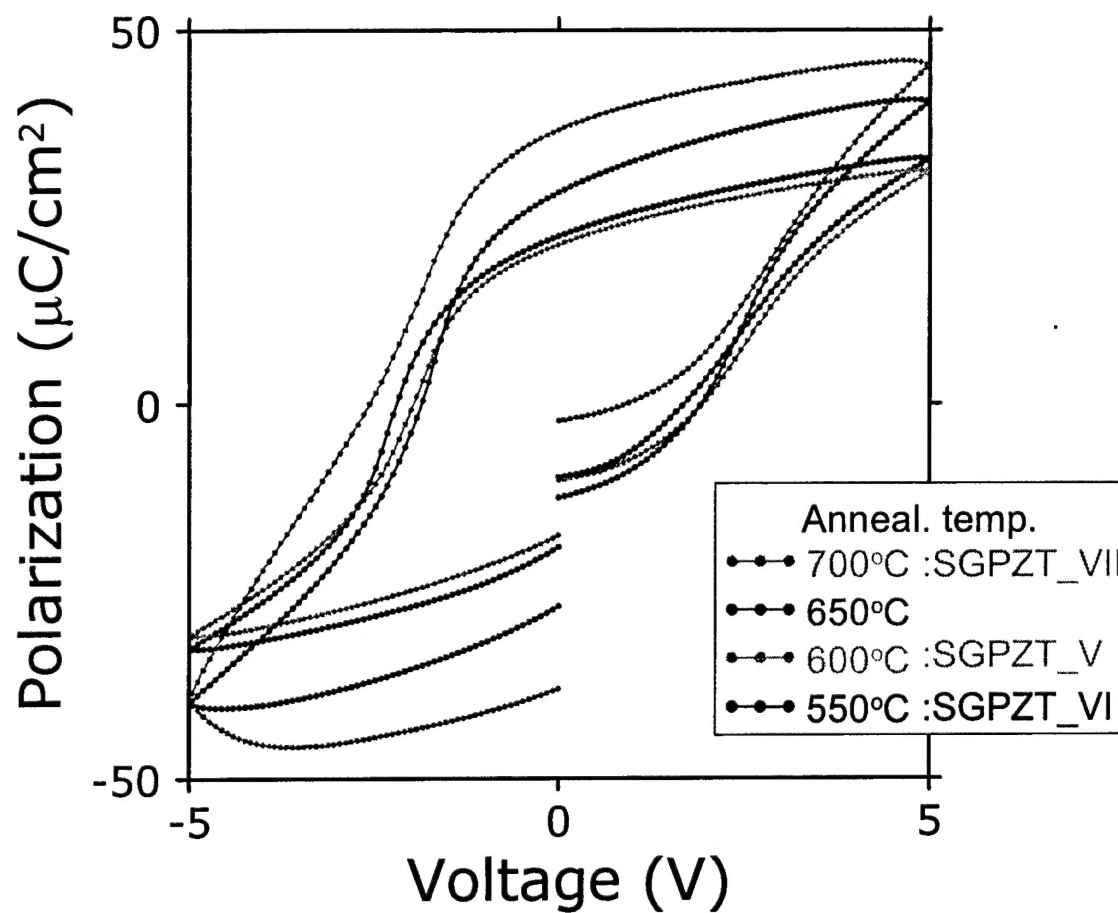


Figure 6. Polarization vs. voltage hysteresis loops of Au/PZT/Ir at various annealing temperature (550, 600, 650, and 700°C) in air for 30 min

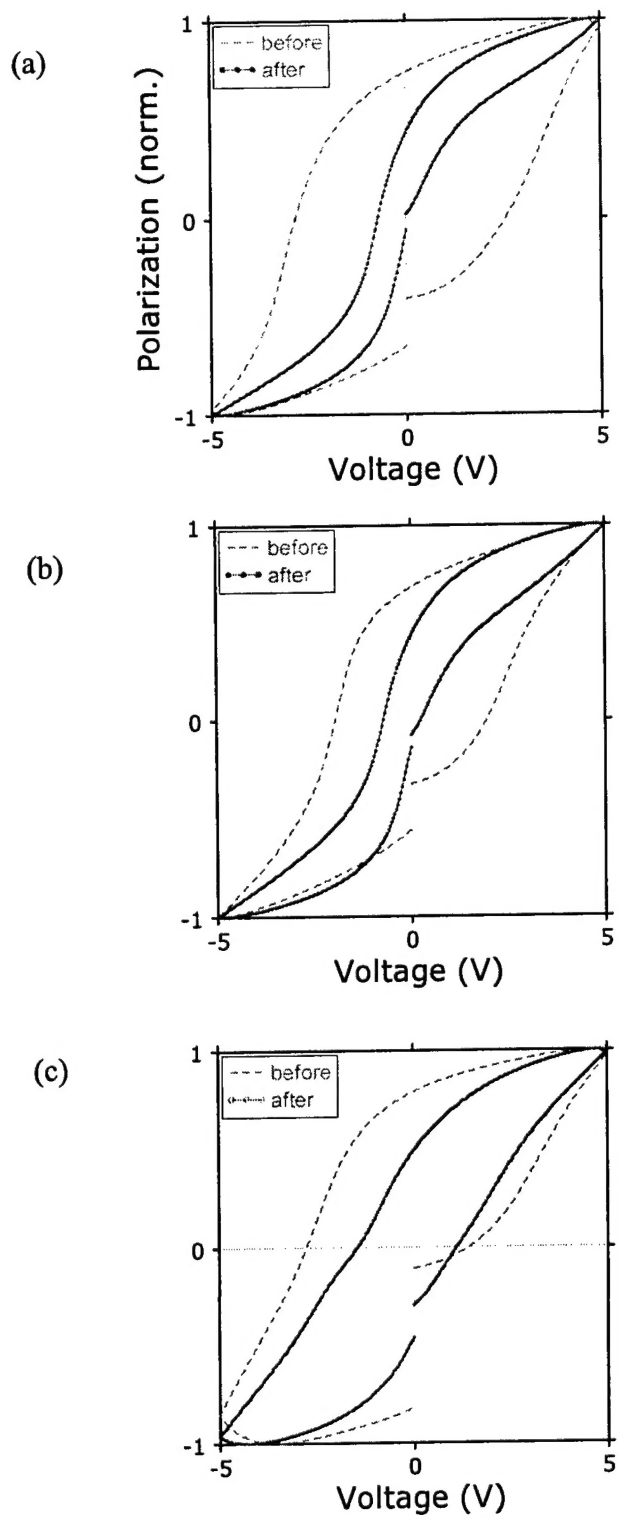


Figure 7. Normalized polarization vs. voltage before and after annealing in  $O_2/Ar$  ambient at  $700^\circ C$  for 10 min: (a) SGPZT\_IV, (b) SGPZT\_V, and (c) SGPZT\_VI.

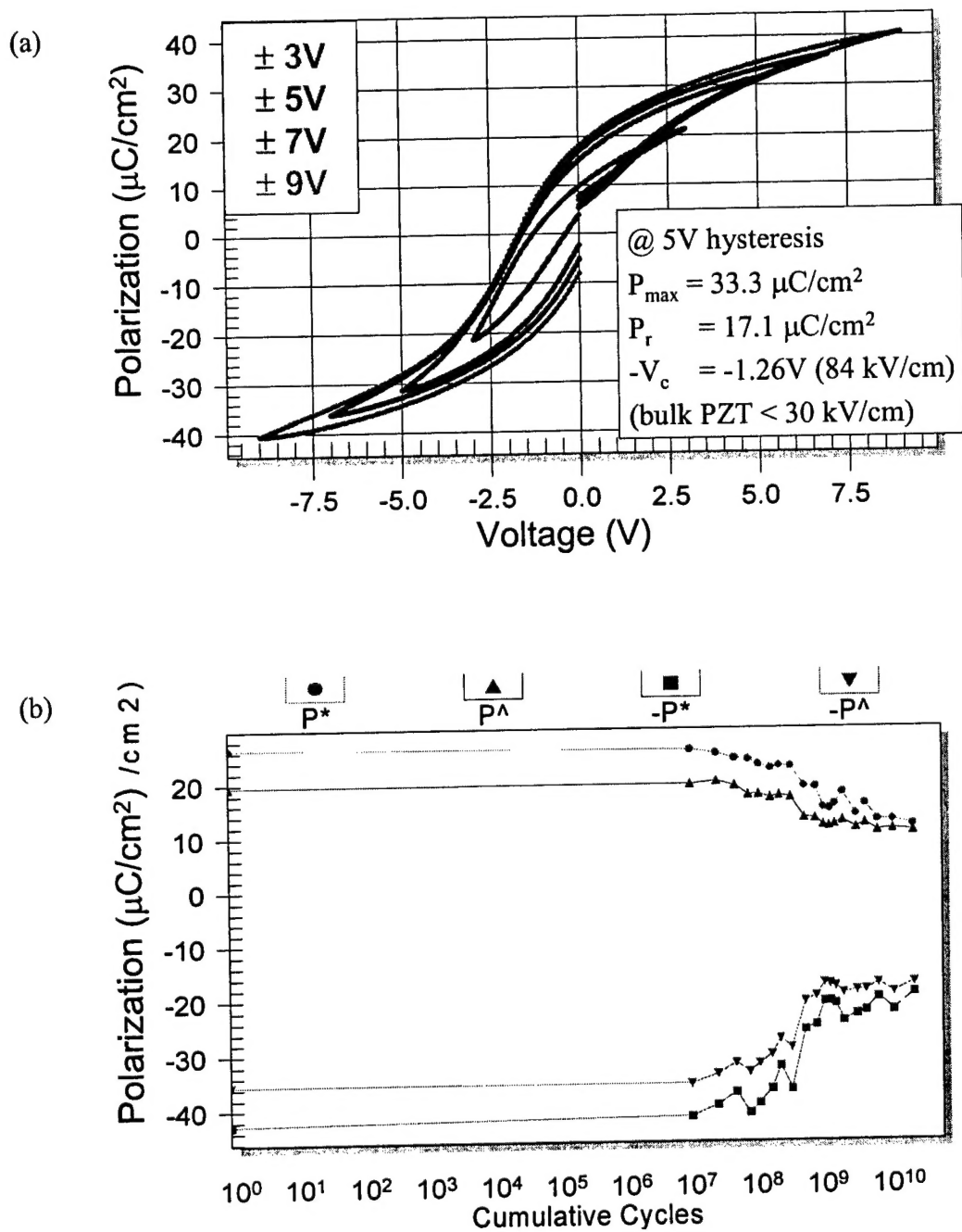


Figure 8. (a) Polarization hysteresis loops of Au/PZT/Pt (600°C, 10 min RTA in air) at various sweep voltage  $\pm 3$ ,  $\pm 5$ ,  $\pm 7$ ,  $\pm 9$  V. (b) Polarization fatigue curves (PUND test), frequency =  $10^6$  Hz.

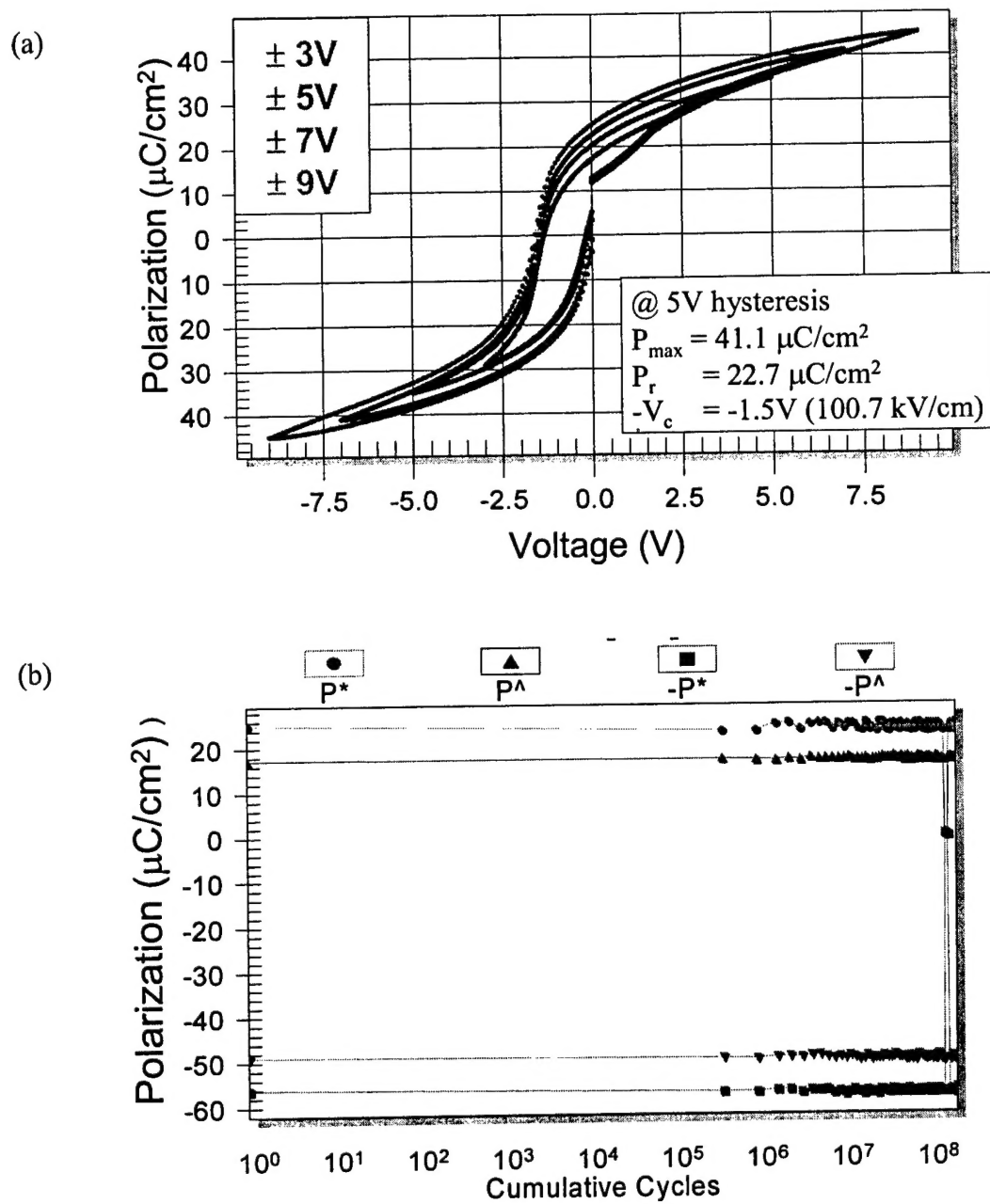


Figure 9. (a) Polarization hysteresis loops of Au/PZT/Ir (600°C, 10 min RTA in air) at various sweep voltage  $\pm 3$ ,  $\pm 5$ ,  $\pm 7$ ,  $\pm 9$  V. (b) Polarization fatigue curves (PUND test), frequency =  $10^6$  Hz